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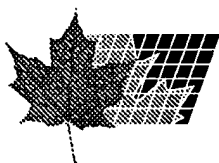
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(54) **MELANGES DE CAOUTCHOUC**  
(54) **RUBBER MIXTURES**

(57) Rubber mixtures which contain an organosilane of the general structure  $R^1R^2R^3Si-R^4-Z$  (I).



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Abstract

Rubber mixtures which contain an organosilane of the general structure  $R^1R^2R^3Si-R^4-Z$  (I).

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**Rubber mixtures**

The present invention relates to rubber mixtures, to a process for their preparation and to the production of  
5 mouldings.

It is known to use sulfur-containing organosilicon compounds, such as 3-mercaptopropyltrimethoxysilane, 3-thiocyanatopropyltriethoxysilane or bis(3-  
10 [triethoxysilyl]propyl)tetrasulfane, as silane coupling agents or reinforcing additives in oxide-filled rubber mixtures, inter alia for the production of treads and other parts of automobile tyres (DE 2 141 159, DE 2 212 239, DE 195 444 69 A1, US 3 978 103,  
15 US 4 048 206, EP 784 072 A1).

The additional use of alkylsilanes in rubber mixtures to lower the mixing viscosity is also known (EP 795 577 A1, EP 864 605 A2).

20

In the preparation of rubber mixtures with organosilanes and a filler, for example a precipitated silicic acid, a chemical reaction takes place during the mixing process, for example in an internal mixer. This chemical reaction  
25 is a condensation reaction which is accompanied by the release of a considerable amount of alcohol. As described in the literature [A. Hunsche, U. Görl, A. Müller, M. Knaack, T. Göbel, *Kautsch. Gummi, Kunstst.* 50, 881 (1997)], this condensation reaction is made up of a  
30 primary reaction, in which an ethoxy group reacts with a silanol group from the silicic acid, and a secondary reaction between two ethoxy groups, which results in crosslinking between the silane molecules. According to the state of the art, up to three mol of ethanol can be

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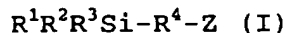
eliminated per mol of silicon by these reactions when silanes containing three ethoxy functional groups are used.

5 In some cases this eliminated alcohol causes appreciable technical problems in the further processing of the rubber mixtures, such as the porosity of the mixture during extrusion or undesired blistering in the rubber itself. Furthermore, it is in the interest of health and the  
10 environment to reduce the amount of alcohol released during the reaction.

It has now been found that these disadvantages of the state of the art can be greatly mitigated by the use of  
15 organosilanes in which the trialkoxysilyl functional group used hitherto is replaced with silyl functional groups containing fewer alkoxy groups.

Accordingly, the present invention relates to the use of  
20 organosilanes of the general structure  $R^1R^2R^3Si-R^4-Z$  (I), it being possible for the organosilane to contain fewer than 3 ethoxy groups per silicon.

The invention provides rubber mixtures which are  
25 characterized in that they contain organosilanes of the general structure



30 wherein  $R^1$ ,  $R^2$  and  $R^3$  independently of one another are H,  $(C_1-C_4)$ alkyl,  $(C_1-C_4)$ alkoxy or halogen and the number of alkyl groups is  $\geq 1$ ;  $R^4$  is a linear or branched  $(C_1-C_{18})$ alkylidene group; and  $Z = H$ ,

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halogen, SCN, SH or  $S_x-R^4-SiR^1R^2R^3$ , it being possible for x to take a value of 2 to 10.

Preferred organosilanes of the type described above are those with dialkylmonoalkoxysilyl functional groups in place of the trialkoxysilyl functional groups conventionally used. Particularly preferred silanes are the bis(3-[dimethylethoxysilyl]polysulfanes) according to the invention.

10

The present invention therefore provides rubber mixtures containing rubber, filler, especially including precipitated silicic acid, optionally other rubber auxiliaries, and at least one organosilane which is built up of the structural units described above and which is used in amounts of 0.1 to 15 wt.%, based on the amount of rubber used.

Because of the smaller number of alkoxy groups in the organosilanes of general structure (I), the unpleasant release of alcohol is reduced when they are used in rubber mixing processes. Compared with the known procedure, e.g. simply using bis(3-[triethoxysilyl]propyl)tetrasulfane (TESPT) as coupling agent, the maximum possible release of alcohol is reduced by 66%.

Surprisingly, it has now also been found that the rubber mixtures prepared with the silanes according to the invention, and the vulcanizates prepared therefrom, do not exhibit any disadvantages in respect of their engineering properties compared with the reference containing a triethoxysilyl functional group, according to the state of the art (Examples 1 and 2).

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The organosilanes according to the invention and the fillers are preferably added at stock temperatures of 100 to 200°C, but they can also be added later at lower temperatures (40 to 100°C), e.g. together with other rubber auxiliaries.

The organosilanes can be introduced into the mixing process either in pure form or adsorbed on an inert organic or inorganic carrier. Preferred carrier materials are silicic acids, natural or synthetic silicates, aluminium oxide or carbon blacks.

The following fillers are suitable for the rubber mixtures according to the invention:

15

- Carbon blacks: The carbon blacks to be used here are prepared by the lamp black, furnace or gas black process and have BET surface areas of 20 to 200 m<sup>2</sup>/g, e.g. SAF, ISAF, HSAF, HAF, FEF or GPF carbon blacks. The carbon blacks can optionally also contain heteroatoms such as Si.

20

- Highly disperse silicic acids, prepared e.g. by the precipitation of silicate solutions or the flame hydrolysis of silicon halides, with specific surface areas of 5 to 1000, preferably 20 to 400 m<sup>2</sup>/g (BET surface area), and with primary particle sizes of 10 to 400 nm. The silicic acids can optionally also take the form of mixed oxides with other metal oxides such as Al, Mg, Ca, Ba, Zn and titanium oxides.

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- Synthetic silicates, such as aluminium silicate, or alkaline earth metal silicates like magnesium silicate

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or calcium silicate, with BET surface areas of 20 to 400 m<sup>2</sup>/g and primary particle diameters of 10 to 400 nm.

- 5     - Natural silicates, such as kaolin and other naturally occurring silicic acids.
- Glass fibres and glass fibre products (mats, strands) or glass microspheres.
- 10    It is preferred to use carbon blacks with BET surface areas of 20 to 400 m<sup>2</sup>/g or highly disperse silicic acids, prepared by the precipitation of silicate solutions, with BET surface areas of 20 to 400 m<sup>2</sup>/g in amounts of 5 to 150 parts by weight, based in each case on 100 parts of
- 15    rubber.

Said fillers can be used on their own or in a mixture. In one particularly preferred embodiment of the process, the mixtures are prepared using 10 to 150 parts by weight of

20   white fillers, optionally together with 0 to 100 parts by weight of carbon black, and 0.3 to 10 parts by weight of a compound of formula (I), based in each case on 100 parts by weight of rubber.

- 25    Apart from natural rubber, synthetic rubbers are also suitable for preparing the rubber mixtures according to the invention. Preferred synthetic rubbers are described for example in W. Hofmann, Kautschuktechnologie (Rubber Technology), Genter Verlag, Stuttgart 1980. They include
- 30    inter alia:

- polybutadiene (BR)
  - polyisoprene (IR)
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- styrene/butadiene copolymers with styrene contents of 1 to 60 wt.%, preferably 2 to 50 wt.% (SBR)
- 5 - isobutylene/isoprene copolymers (IIR)
- butadiene/acrylonitrile copolymers with acrylonitrile contents of 5 to 60 wt.%, preferably 10 to 50 wt.% (NBR)
- 10 - partially hydrogenated or fully hydrogenated NBR (HNBR)
- ethylene/propylene/diene copolymers (EPDM)

and mixtures of these rubbers. Anionically polymerized  
15 solution SBRs with a glass transition temperature above -50°C, and mixtures thereof with diene rubbers, are of particular interest for the production of automobile tyres.

- 20 The rubber vulcanizates according to the invention can contain other rubber auxiliaries known to the rubber industry, such as reaction accelerators, antioxidants, heat stabilizers, light stabilizers, antiozone agents, processing aids, plasticizers, tackifiers, blowing agents,  
25 dyes, pigments, waxes, extenders, organic acids, retarders, metal oxides, and activators such as triethanolamine, polyethylene glycol and hexanetriol.

The rubber auxiliaries are used in conventional amounts,  
30 which depend inter alia on the intended use. Conventional amounts are e.g. amounts of 0.1 to 50 wt.%, based on rubber. The organosilanes with rubber-reactive groups can be used on their own as crosslinking agents. It is normally advisable to add other crosslinking agents.

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Other known crosslinking agents which can be used are sulfur or peroxides. The rubber mixtures according to the invention can also contain vulcanization accelerators, examples of suitable vulcanization accelerators being mercaptobenzthiazoles, sulfenamides, guanidines, thiurams, dithiocarbamates, thioureas and thiocarbonates. The vulcanization accelerators and the sulfur or peroxides are used in amounts of 0.1 to 10 wt.%, preferably 0.1 to 5 wt.%, based on rubber.

10

The vulcanization of the rubber mixtures according to the invention can be carried out at temperatures of 100 to 200°C, preferably 130 to 180°C, optionally under a pressure of 10 to 200 bar. The rubbers can be mixed with the filler, the rubber auxiliaries, if appropriate, and the silanes of general structure (I) in conventional mixers such as rolls, internal mixers and mixer-extruders. The rubber vulcanizates according to the invention are suitable for the production of mouldings, e.g. for the manufacture of pneumatic tyres, tyre treads, cable sheathing, hosing, transmission belts, conveyor belts, roll covers, tyres, shoe soles, gaskets and damping elements.

25 **Examples: Preparation of rubber mixtures and vulcanizates**

#### **General operating instructions**

The rubber mixture is prepared in two stages in an internal mixer (Werner & Pfleiderer GK1.5N) with mixing times of 6 and 5 minutes at a speed of rotation of 60-70 rpm up to a discharge temperature of max. 155°C, followed by a mixing stage in an internal mixer at max.

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90°C, the formulation being as indicated in Table 1 below, where the unit phr denotes parts by weight based on 100 parts of raw rubber used.

- 5 General processes for the preparation of rubber mixtures and vulcanizates thereof are described for example in "Rubber Technology Handbook", W. Hofmann, Hanser Verlag 1994.
  - 10 The vulcanization times at 165°C are 16 and 30 minutes for the test pieces of Examples 1 and 2 respectively.
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Table 1

Substance	Amount [phr]
1st stage	
Buna VSL 5025-1	96.0
Buna CB 24	30.0
Ultrasil VN3	80.0
ZnO	3.0
Stearic acid	2.0
Naftolen ZD	10.0
Vulkanox 4020	1.5
Protector G35P	1.0
Silane	acc. to Ex. 1, 2
2nd stage	
Batch stage 1	
3rd stage	
Batch stage 2	
Perkacit TBZTD	0.2
Vulkacit D	2.0
Vulkacit CZ	1.5
Sulfur	1.5

The polymer VSL 5025-1 is a solution-polymerized SBR copolymer from Bayer AG with a styrene content of 25 wt.% and a butadiene content of 75 wt.%. Of the butadiene, 73% is 1,2-linked, 10% cis-1,4-linked and 17% trans-1,4-linked. The copolymer contains 37.5 phr of oil and has a Mooney viscosity (ML 1+4/100°C) of 50 ± 5.

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The polymer Buna CB 24 is a cis-1,4-polybutadiene (neodymium type) from Bayer AG with a cis-1,4 content of 97%, a trans-1,4 content of 2%, a 1,2 content of 1% and a Mooney viscosity of between 39 and 49.

5

The silicic acid VN3 from Degussa AG has a BET surface area of 175 m<sup>2</sup>/g. TESP (bis(3-[triethoxysilyl]propyl)disulfane) of Reference Example 1 is prepared according to patent D 195 414 04. The silane of Example 2, bis(3-[dimethylethoxysilyl]propyl)disulfane, is prepared according to the state of the art by the hydrosilylation of chlorodimethylsilane with allyl chloride, followed by ethanolysis and sulfurization analogously to the process indicated in patent D 197 342 95 A1.

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The aromatic oil used is Naftolen ZD from Chemetall. Vulcanox 4020 is PPD from Bayer AG and Protektor G35P is an antiozone wax from HB-Fuller GmbH. Vulkacit D (DPG) and Vulkacit CZ (CBS) are commercial products from Bayer AG. Perkacit TBZTD is a commercial product from Flexis S.A.

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The engineering properties of the rubber are tested by the methods indicated in Table 2.

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Table 2

Physical test	Standard / Conditions
ML 1+4, 100°C	DIN 53523/3, ISO 667
Vulcameter test, 165°C	DIN 53529/3, ISO 6502
Ring tensile test, 23°C Tensile strength Tensile stresses Elongation at break	DIN 53504, ISO 37
Shore A hardness, 23°C	DIN 53 505
Ball rebound, 0, 23 and 60°C	ASTM D 5308
Viscoelast. prop., 0 and 60°C E* tan $\delta$	DIN 53 513, ISO 2856
DIN abrasion, 10 N force	DIN 53 516
Dispersion	ISO/DIS 11345

**Examples 1 and 2:**

- 5 Example 1 (Comparative Example) and Example 2 are carried out in accordance with the general operating instructions.

As distinct from Comparative Example 1 with 5.8 phr of TESPD, 4.3 phr of bis(3-

- 10 [dimethylethoxysilyl]propyl)disulfane, corresponding to an equimolar dosage, are added to the mixture of Example 2. The engineering data for the raw rubber mixture and the vulcanizate are as follows (Table 3):

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Table 3

Raw mixture			
Characteristic	Unit	Ex. 1	Ex. 2
ML (1+4) (3rd stage)	[MU]	69	74
MDR, 165°C			
Dmax-Dmin	[dNm]	14.1	13.8
t 10%	[min]	2.4	3.1
Vulcanizate			
Characteristic	Unit	Ex. 1	Ex. 2
<b>Ring tensile test</b>			
Tensile strength	[MPa]	16.3	17.1
Tensile stress at 100% elongation	[MPa]	1.5	1.6
Tensile stress at 300% elongation	[MPa]	6.2	6.4
Elongation at break	[%]	540	560
Shore A hardness	[SH]	60	59
DIN abrasion	[mm <sup>3</sup> ]	100	110
Ball rebound (0°C)	[%]	12.5	11.6
Ball rebound (23°C)	[%]	34.3	32
Ball rebound (60°C)	[%]	59.8	59.4
<b>Dynamic testing</b>			
Dyn. modulus E* (0°C)	[MPa]	16.7	17.1
Dyn. modulus E* (60°C)	[MPa]	7.3	7.3
Modulus loss factor tan $\delta$ (0°C)	[-]	0.444	0.476
Modulus loss factor tan $\delta$ (60°C)	[-]	0.143	0.131
Dispersion	[-]	6	6

The data in Table 3 prove that the use of the dimethylethoxysilane according to the invention (Ex. 2)

5 causes no impairment of the engineering properties of the

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rubber compared with triethoxysilane according to the state of the art (Ex. 1). Rather, there is actually an advantage in the reduced value of  $\tan \delta$  (60°C), which correlates with the rolling resistance.

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## Claims

1. Rubber mixtures, characterized in that they contain organosilanes of the general structure

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wherein  $R^1$ ,  $R^2$  and  $R^3$  independently of one another are H,  $(C_1-C_4)$ alkyl,  $(C_1-C_4)$ alkoxy or halogen and the number of alkyl groups is  $\geq 1$ ;  $R^4$  is a linear or branched  $(C_1-C_{18})$ alkylidene group; and  $Z = H$ , halogen, SCN, SH or  $S_x-R^4-SiR^1R^2R^3$ , it being possible for  $x$  to take a value of 2 to 10.

15

2. Rubber mixtures according to Claim 1, characterized in that they contain an organopolysulfanesilane and an organoalkylsilane.

- 20 3. Rubber mixtures according to Claims 1 and 2, characterized in that they contain the organosilanes in an amount of 0.1 to 15 wt.%, based on the amount of rubber used.

- 25 4. Rubber mixtures according to Claims 1 to 3, characterized in that the organopolysulfanesilane is a silane in which:

$R^1 =$  ethoxy or methoxy,  $R^2 = R^3 =$  methyl,  $R^4 =$  propyl or isobutyl and  $Z = S_x-R^4-SiR^1R^2R^3$ ,  $x$  having a statistical mean value of 2 to 4.

30

5. Rubber mixtures according to Claims 1 to 4, characterized in that the organoalkylsilane is a silane in which:

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$R^1$  = ethoxy or methoxy,  $R^2 = R^3$  = methyl and  $R^4$  =  $(C_1-C_{18})$  alkyl.

6. Rubber mixtures according to Claims 1 to 5,  
5 characterized in that they contain a synthetic rubber, a silicic acid as filler and one of the following two organosilanepolysulfanes: bis(3-[dimethylethoxysilyl]propyl)tetrasulfane or bis(3-[dimethylethoxysilyl]propyl)disulfane.  
10
7. Rubber mixtures according to Claims 1 to 6,  
characterized in that they contain a synthetic rubber, a silicic acid as filler, one of the following two organosilanepolysulfanes: bis(3-[dimethylethoxysilyl]propyl)tetrasulfane or bis(3-[dimethylethoxysilyl]propyl)disulfane, and an  
15 alkylsilane.
8. Process for the preparation of rubber mixtures  
20 according to Claims 1 to 7 which contain at least one other filler in addition to the rubber, characterized in that an organosilanepolysulfane according to one of Claims 1 to 4 is used.
- 25 9. Process for the preparation of rubber mixtures which contain at least one other filler in addition to the rubber, characterized in that an organosilanepolysulfane and an organoalkylsilane according to one of Claims 1, 4 and 5 are used.  
30
10. Moulding obtainable from a rubber mixture according to one of Claims 1 to 7.

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11. Moulding according to Claim 10, characterized in that  
it is a pneumatic tyre.

12. Moulding according to Claim 10, characterized in that  
5 it is a tyre tread.

13. Use of the rubber mixtures according to one of Claims  
1 to 7 for the production of mouldings, especially  
pneumatic tyres or tyre treads.

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